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The H_2SO_4-HNO_3-NH_3 System at High Humidities and in Fogs 2. Comparison of Field Data With Thermodynamic Calculations

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Concentrations of HNO_3(g) and NH_3(g) determined in the field were compared to predictions from aerosol equilibrium models. The products of HNO_3(g) and NH_3(g) concentrations measured under cool and humid nonfoggy conditions agreed in magnitude with predictions from a comprehensive thermodynamic model for the atmospheric H_2SO_4-HNO_3-NH_3-H_2O system. Observed concentrations of NH_3(g) in fogs were generally consistent with those predicted at equilibrium with fog water, but important discrepancies were noted in some cases. These discrepancies may be due to fluctuations in fog water composition over the course of sample collection or to the sampling of nonfoggy pockets of air present within the fog. Detectable concentrations of HNO_3(g) (up to 23 neq m^{-3}) were often found in fogs with pH < 5 and were attributed to the sampling of nonfoggy air or to the slow rate of HNO_3(g) diffusion to fog droplets. Concentrations of HNO_3(g) in fogs with pH > 5 were below the detection limit of 4–8 neq m^{-3}.

INTRODUCTION

The chemical speciation of the H_2SO_4-HNO_3-NH_3-H_2O system between atmospheric phases has been the subject of much recent interest. Sulfuric acid nucleates with water vapor under usual atmospheric conditions [*Kiang et al.*, 1973], but HNO_3 remains in the gas phase at relative humidities up to about 98% [*Nair et al.*, 1983]. Ammonia is scavenged by acidic sulfate aerosols until eventual neutralization is achieved; however, it has a substantial vapor pressure over ammonium nitrate aerosol. A key question to our understanding of aerosol nitrate formation is the determination of NH_3 and HNO_3 vapor pressures over aerosol formed from H_2SO_4-HNO_3-NH_3 atmospheric mixtures.

A number of thermodynamic models have attempted to answer that question. *Tang* [1980] and *Stelson and Seinfeld* [1982*a*] studied the effect of relative humidity and pH on the vapor pressures of HNO_3 and NH_3 over their aqueous solutions. *Stelson and Seinfeld* [1982*b*] determined the dependence on temperature and relative humidity of the ammonium nitrate aerosol dissociation constant $K = P_{HNO_3} \times P_{NH_3}$ and later reported [*Stelson and Seinfeld*, 1982*c*] that addition of H_2SO_4 to the mixture does not lower K greatly unless the H_2SO_4/HNO_3 ratio is very large. *Saxena et al.* [1983] and *Bassett and Seinfeld* [1983, 1984] proposed comprehensive multiphase thermodynamic models for the H_2SO_4-HNO_3-NH_3-H_2O system.

All of the above models are basically consistent one with the other and represent various degrees of sophistication in the treatment of the H_2SO_4-HNO_3-NH_3 system. The Bassett and Seinfeld models offer at present the greatest level of chemical detail. In these models the equilibrium composition is calculated by minimizing the Gibbs free energy of a system composed of the gas phase species H_2SO_4(g), HNO_3(g), and NH_3(g); the aqueous phase species H^+, HSO_4^-, SO_4^{2-}, NO_3^-, and NH_4^+; and the solid phases NH_4HSO_4(s), $(NH_4)_3H(SO_4)_2$(s), $(NH_4)_2SO_4$(s), NH_4NO_3(s), $(NH_4)_2SO_4 \cdot 3NH_4NO_3$(s), and $(NH_4)_2SO_4 \cdot 2NH_4NO_3$(s). The *Bassett and Seinfeld* [1984] model considers in addition the increase in vapor pressure due to the Kelvin effect and thus predicts the size distribution of NO_3^- aerosol from the size distribution of SO_4^{2-} aerosol. The *Bassett and Seinfeld* [1983] model ignores the Kelvin effect, but this is reported to cause only a negligible underestimate of K. In the special case of the HNO_3-NH_3-H_2O system the *Bassett and Seinfeld* [1983] model reduces to the *Stelson and Seinfeld* [1982*b*] model, which uses the same thermodynamic data and ionic strength correction procedures.

The hygroscopic aerosol is an aqueous solution at high humidities, and Table 1 gives the reactions determining the speciation of HNO_3 and NH_3 under those conditions. K decreases rapidly with increasing humidity above the deliquescence point [*Stelson and Seinfeld*, 1982*b*]. Above 100% relative humidity, fog droplets form by activation of condensation nuclei, resulting in a considerable increase of the atmospheric liquid water content and a corresponding enhancement of HNO_3 and NH_3 heterogeneous condensation. Fog droplets are not at stable equilibrium with the surrounding water vapor, and thermodynamic models predicting K as a function of relative humidity cannot be applied; however, HNO_3(g) and NH_3(g) concentrations at equilibrium with the fog water can be directly calculated from measured fog water concentrations. Fog droplets are sufficiently dilute solutions that the Debye-Hückel expression for activity coefficients [*Stumm and Morgan*, 1981] is appropriate.

In fogs the equilibrium partitioning of HNO_3 and NH_3 between the gas phase and the fog water can be determined from the liquid water content, the fog water pH, and (R1)–(R3). Liquid water contents in fog range from 0.01–1 g m^{-3}, and fog water pH values have been found to range from about 2 to 8 [*Munger et al.*, 1983; *Jacob et al.*, this issue]. Over 99% of total HNO_3 at equilibrium with fog water is scavenged as NO_3^- in this range of conditions (reaction (R1)). No measurable HNO_3(g) should therefore be found at equilibrium in fog, even acidic fog. On the other hand, the equilibrium speciation of NH_3 is strongly dependent on droplet pH, liquid water content, and temperature. The fraction F of total NH_3 scavenged by fog is given by:

$$F = \frac{LRTK_2[1 + (K_3[H^+])]}{1 + LRTK_2[1 + (K_3[H^+])]} \quad (1)$$

where the equilibrium constants K_2 and K_3 are the K_{298} values of Table 1 corrected for temperature with the Van't

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TABLE 1. Dissociation and Vapor Pressure Equilibria of HNO_3 and NH_3

Reaction Number	Reaction	K_{298}, kcal mol^{-1}	ΔH_{298}, kcal mol^{-1}	Reference
(R1)	$HNO_3(g) = NO_3^- + H^+$	$3.2 \times 10^6\ M^2\ atm^{-1}$	−17.3	*Schwartz and White* [1981]
(R2)	$NH_3(g) = NH_3(aq)$	$7.4 \times 10^1\ M\ atm^{-1}$	−6.8	*Hales and Drewes* [1979]
(R3)	$NH_3(aq) + H^+ = NH_4^+$	$1.7 \times 10^9\ M^{-1}$	−12.5	*Smith and Martell* [1976]

Hoff equation, L is the liquid water content (cubic meters of water per cubic meter of air), R is the gas constant (8.20568×10^{-2} L atm mol^{-1} K^{-1}), and T is the absolute temperature. Note that in the derivation of (1) the Debye-Hückel activity coefficients cancel each other. F is plotted in Figure 1 as a function of pH under various conditions.

The thermodynamic approaches outlined above provide simple ways for treating aerosol formation and composition in atmospheric chemistry models; therefore it is important to determine the accuracy with which they can describe real atmospheric conditions. The model of *Stelson and Seinfeld* [1982*b*] has been tested with field data in three studies [*Stelson and Seinfeld*, 1982*b*; *Harrison and Pio*, 1983; *Hildemann et al.*, 1984], which all reported that the products of measured $HNO_3(g)$ and $NH_3(g)$ concentrations agreed in magnitude with predicted values of K. *Tanner* [1983] found that the model of *Tang* [1980] adequately predicted concentrations of $HNO_3(g)$ and $NH_3(g)$ over dry aerosol, but he found large discrepancies at high humidities between his field data and the model of *Tang* [1980] for vapor pressures over aqueous aerosol. *Bassett and Seinfeld* [1983] reexamined the data of *Tanner* [1983] in light of their own model and again noted large discrepancies at high humidities between model and observations. No further tests of the *Bassett and Seinfeld* [1983] model have been reported to date.

Measurements of $HNO_3(g)$ and $NH_3(g)$ in fogs or clouds are few. *Daum et al.* [1984] found concentrations of both gases to be below the detection limit of 0.4 ppb (17 neq m^{-3}) in acidic stratus clouds (pH 3.2–4.2). No measurements are available in nonacidic fogs, where NH_3 should have a substantial vapor pressure. *Ayers et al.* [1984] have compared measured ground level $NH_3(g)$ concentrations to those predicted from $[H^+]$ and $[NH_4^+]$ rainwater concentrations and reported large discrepancies between the two.

Over the course of an extensive sampling program in the wintertime atmosphere of the San Joaquin Valley of California [*Jacob et al.*, this issue], we determined $HNO_3(g)$ and $NH_3(g)$ concentrations simultaneously with aerosol and fog water composition. In this paper we compare the concentrations of $HNO_3(g)$ and $NH_3(g)$ determined under nonfoggy conditions to those predicted by the *Bassett and Seinfeld* [1983] model for the H_2SO_4-HNO_3-NH_3-H_2O system. Our data is well suited for such a comparison because the ions SO_4^{2-}, NO_3^-, and NH_4^+ contributed over 90% of the ionic content of the aerosol. In fogs we compare measured concentrations of $HNO_3(g)$ and $NH_3(g)$ to those expected at equilibrium with the fog water concentrations; fog water pH values ranged from 2.9 to 7.6, thus spanning a broad range of predicted $NH_3(g)$-scavenging efficiencies (Figure 1).

Gaseous HNO_3 and NH_3 were determined by dual-filter methods [*Russell and Cass*, 1984]. Aerosol was collected on an open-faced Teflon filter surmounted by a cover to prevent collection of large particles by sedimentation. Fog water was collected with a rotating arm collector [*Jacob et al.*, 1984]. The reader is referred to *Jacob et al.* [this issue] for a description of sampling sites, analytical methods, and a detailed analysis of measurement errors and biases associated with our sampling techniques.

We will generally present $HNO_3(g)$ and $NH_3(g)$ concentrations in units of equivalents per cubic meter, for consistency with the units of NO_3^- and NH_4^+ aerosol concentrations. "Equivalent" in that sense refers to the proton donor or acceptor capacity of the gas when scavenged by the aerosol. Both $HNO_3(g)$ and $NH_3(g)$ contribute one equivalent per mole; 1 ppb = 43 neq m^{-3} at 5°C.

NONFOGGY CONDITIONS

The main site of the San Joaquin Valley sampling program was located in Bakersfield, California. The Bakersfield data are given in Table 2. For comparison with the *Bassett and Seinfeld* [1983] model the aerosol compositions were reduced to model mixtures of SO_4^{2-}, NO_3^-, NH_4^+, and H^+. This was done by assuming concentrations of H^+ and OH^- to satisfy electroneutrality with the measured concentrations of SO_4^{2-}, NO_3^-, and NH_4^+. The presence of other ions in the real aerosol will perturb the thermodynamics, but this perturbation should be small because the ions SO_4^{2-}, NO_3^-, and NH_4^+ contributed over 90% of the total aerosol ionic content [*Jacob et al.*, this issue]. Aerosol concentrations of HCO_3^- and $RCOO^-$ were not determined, but the balances of NH_4^+ to $(NO_3^- + SO_4^{2-})$ in Table 2 show no evidence of excess NH_4^+ attributable to HCO_3^- or $RCOO^-$ ammonium salts. Alkaline ammonium salts appear to be volatile under nonfoggy conditions [*Jacob et al.*, this issue]. Therefore the $(SO_4^{2-}, NO_3^-, NH_4^+, H^+)$ mixture is an adequate model for the ionic content of the Bakersfield aerosol.

We applied the *Bassett and Seinfeld* [1983] model to describe two different partitioning modes for SO_4^{2-} and NO_3^-: (1) SO_4^{2-} and NO_3^- present exclusively in different aerosol phases ("external mixture"), and (2) SO_4^{2-} and NO_3^- al-

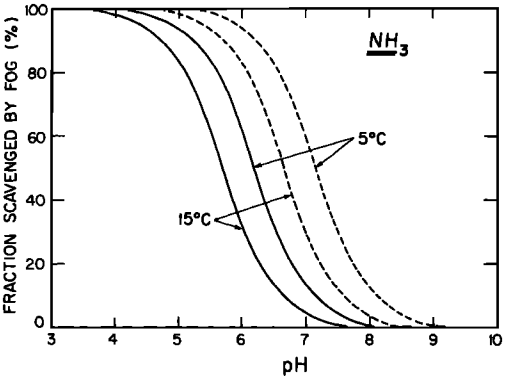

Fig. 1. Fraction of NH_3 scavenged by fog water at equilibrium. All fog droplets are assumed to be at the same pH. Liquid water contents of 0.05 g m^{-3} (solid line) and 0.5 g m^{-3} (dashed line) are considered.

TABLE 2. Bakersfield 1983–1984 Data for Aerosol and Gaseous H_2SO_4-HNO_3-NH_3 Species

Date	Time	NH_4^+	NO_3^-	SO_4^{2-}	NH_3(g)	HNO_3(g)	Temperature, °C	Relative Humidity, %
Dec. 31	0000–0345	573	351	351	19	17	7.8 ± 0.9	96
	1200–1610	669	467	297	158	4	10.8 ± 0.6	93
Jan. 1	0215–0815	242	170	89	212	<4	10.4 ± 0.6	96
	1200–1615	275	161	161	68	35	13.3 ± 0.7	76
Jan. 2	0000–0415	273	168	109	67	14	7.2 ± 1.1	89
	1200–1620	344	201	124	107	25	11.8 ± 0.7	74
Jan. 3	0000–0415	545	370	226	483	<4	9.1 ± 0.8	87
	1200–1615	769	445	445	113	11	9.2 ± 0.6	81
Jan. 4	1200–1700	1057	427	660	55	24	9.9 ± 1.3	80
Jan. 5	0100–0510	1141	442	731	63	6	6.9 ± 0.8	95
	1200–1615	923	362	596	60	19	8.8 ± 0.6	85
Jan. 6	0000–0415	1149	388	855	47	7	7.4 ± 0.6	95
Jan. 8	0000–0405	272	142	118	52	6	6.8 ± 0.6	95
Jan. 9	1420–1825	260	85	219	139	8	7.3 ± 0.6	86
Jan. 10	0000–0415	621	117	570	60	46	6.2 ± 0.6	89
	1200–1615	533	152	417	48	14	6.9 ± 0.8	85
Jan. 11	1200–1615	144	105	78	65	46	9.0 ± 0.7	71
Jan. 12	0000–0415	345	204	149	157	<4	3.0 ± 0.9	91
	1200–1615	331	244	169	334	26	11.2 ± 1.0	66
Jan. 13	0000–0400	486	283	407	208	<4	4.6 ± 0.7	96
	0700–1115	729	349	475	122	6	5.9 ± 0.8	91
	1200–1615	855	437	507	240	14	9.9 ± 1.1	73
	1800–2210	692	402	306	161	10	6.4 ± 0.8	85
Jan. 14	0050–0410	567	423	229	180	5	4.9 ± 1.2	89
	0735–1130	641	423	214	470	6	6.4 ± 1.0	85
	1200–1615	318	263	129	118	43	10.7 ± 1.5	61

Complete aerosol analyses are reported by *Jacob* [1985*a*].

Values are in nanoequivalents per cubic meter unless otherwise indicated; time is local time (PST); and relative humidity is calculated from temperature and dew point.

lowed in the same aerosol phases ("internal mixture"). The actual partitioning will lie somewhere between these two extremes, depending on the aerosol formation processes, the kinetics of coagulation, and the Kelvin effect on HNO_3 vapor pressure [*Bassett and Seinfeld*, 1984]. Since NH_4^+ was always in excess of SO_4^{2-}, the external mixture case was treated by assuming that all SO_4^{2-} was present as $(NH_4)_2SO_4$ and solving the equilibrium problem for the remaining HNO_3 and NH_3 with no SO_4^{2-} present. The internal mixture case was treated by directly solving the equilibrium problem for the H_2SO_4-HNO_3-NH_3-H_2O atmospheric system. The presence of SO_4^{2-} and NO_3^- in the same aqueous phase increases the solubility of HNO_3 and NH_3, compared to an external mixture [*Stelson and Seinfeld*, 1982*c*].

Samples were collected over 4-hour sampling periods, during which temperatures and relative humidities remained stable because of the prevalent low-overcast conditions (Table 2). Temperature and dew point were measured hourly at the National Weather Service (NWS) station 8 km north of the Bakersfield sampling site, and standard deviations for temperature over the 4-hour period were calculated from the hourly temperature record; 0.5°C was added to the standard deviation to account for the sensitivity of the readings. The dew point did not change significantly over the 4-hour sampling periods. A few temperature measurements taken at our sampling site were within 1°C of those taken by NWS. Measurements by the NWS confirm that temperatures and relative humidities at the NWS station are representative of those found at our Bakersfield site (D. Gudgel, Bakersfield NWS, private communication, 1984).

The *Bassett and Seinfeld* [1983] model was run with the computer code provided by *Bassett* [1984]. This code required as input the total (gas plus aerosol) concentrations of H_2SO_4, HNO_3, and NH_3, the temperature, and the relative humidity. To calculate the errors on the predictions from the errors on the measurements, 100 sets of input variables were generated for each data point from a random scheme based on the observed values and standard errors for each of the variables; standard errors on the experimental determinations of concentrations were taken from *Jacob et al.* [this issue]. The expected values and standard errors for the output variables were determined from the outputs for the 100 sets of input variables. Results are shown in Figures 2*a* and 2*b*. The aerosol was predicted to be entirely aqueous except in a few cases (indicated on Figures 2*a* and 2*b*). The standard errors on the predicted values of K were mostly due to errors on the determinations of temperature and relative humidity; they were not affected by errors on H_2SO_4, HNO_3, and NH_3 concentrations in the external mixture assumption and were affected only very weakly in the internal mixture assumption. On the other hand, errors on the concentrations of the individual gases were strongly affected by errors on the determinations of concentrations, especially when a close balance existed between total NH_3 and total acids ($HNO_3 + H_2SO_4$). In those cases error bars were very large.

The products of partial pressures observed in the field agreed in magnitude with the values of K predicted by the model. However, the model predictions were consistently too low. Predictions with the external mixture assumption were closer to observations than with the internal mixture assumption. The model appeared to give better predictions for individual gases than for K, but this is deceiving. First, the errors on the predicted gas concentrations were large. Second, K was often so small that one of the gases was almost entirely depleted, and the remaining gas was then simply present at its concentration in excess of the neutralized aerosol.

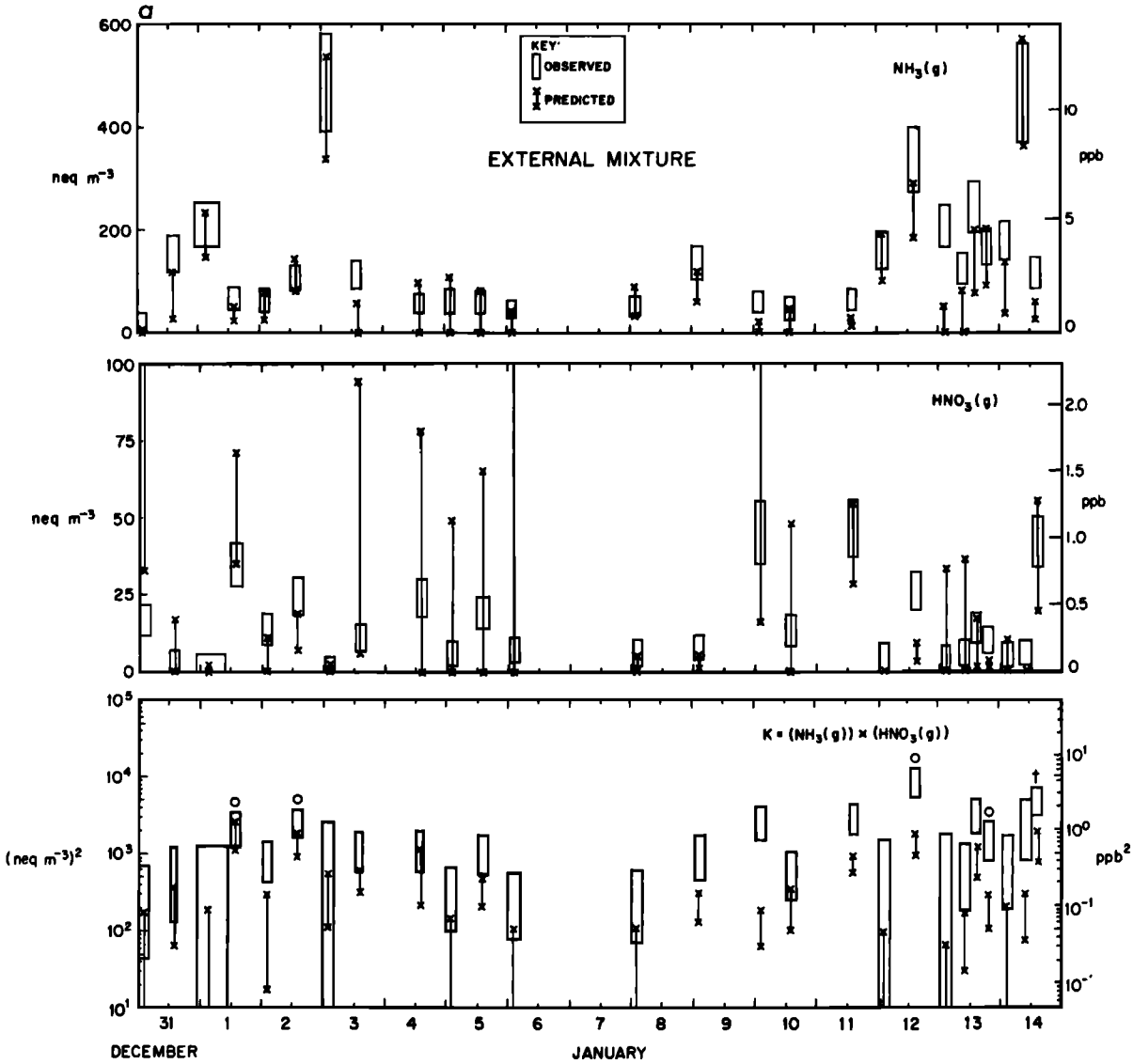

Fig. 2. Comparison of Bakersfield field data to the *Bassett and Seinfeld* [1983] aerosol equilibrium model: concentration products (HNO_3(g)) × (NH_3(g)), and individual concentrations of HNO_3(g) and NH_3(g). Results are given as error bars extending between the limits (mean $-\sigma$) and (mean $+\sigma$). The aerosol was predicted by the model to be an aqueous solution except when indicated by mixed aqueous-solid (open circle), or solid (dagger). Two limiting cases were considered: (*a*) SO_4^{2-} and NO_3^- present exclusively in different aerosol phases (external mixture assumption) and (*b*) SO_4^{2-} and NO_3^- allowed in the same aerosol phases (internal mixture assumption).

Stelson and Seinfeld [1982*b*] also found that the products of vapor pressures over aqueous aerosol were systematically underpredicted by their model, by factors similar to the ones we observed. *Harrison and Pio* [1983] did not find such a systematic trend, although their determinations may have been subject to large errors because of the considerable fluctuations in temperatures and relative humidities over the course of the sampling periods. Because of the many complicated processes occurring in the atmosphere it is difficult to assess the significance of the model underpredictions. Consideration of droplet curvature would increase the predicted K, but *Bassett and Seinfeld* [1984] found this increase to be negligible. Laboratory data of vapor pressures over concentrated ammonium nitrate solutions should provide a check on the accuracy of the thermodynamic calculations, but they are unavailable at this time.

The dual-filter method is known to be subject to positive interferences, that is, concentrations of HNO_3(g) and NH_3(g) may be overestimated [*Appel et al.*, 1980]. Volatilization of NH_4NO_3 from the Teflon prefilter leads to artifact HNO_3(g) and NH_3(g), but in our case this problem is minimized because temperatures and relative humidities remained stable over the course of the sampling periods (Table 2). Another source of positive interference is the displacement of NO_3^- or NH_4^+ by nonvolatile material collected on the filter, for example, acid sulfates or alkaline carbonates. However, if such dispacement reactions occurred on the filter, this would mean that the atmosphere itself was not at equilibrium; in that case, HNO_3(g) and NH_3(g) atmospheric concentrations could have differed substantially from their equilibrium values.

Indeed, a possible explanation for the discrepancies observed is that the atmosphere was not at chemical equilibrium. The NH_3 observed at Bakersfield originated mostly from local ground level sources [*Jacob et al.*, this issue]; HNO_3 and NH_3 may not have had time to mix sufficiently for equilibrium to be achieved. The incorporation of HNO_3(g) and NH_3(g)

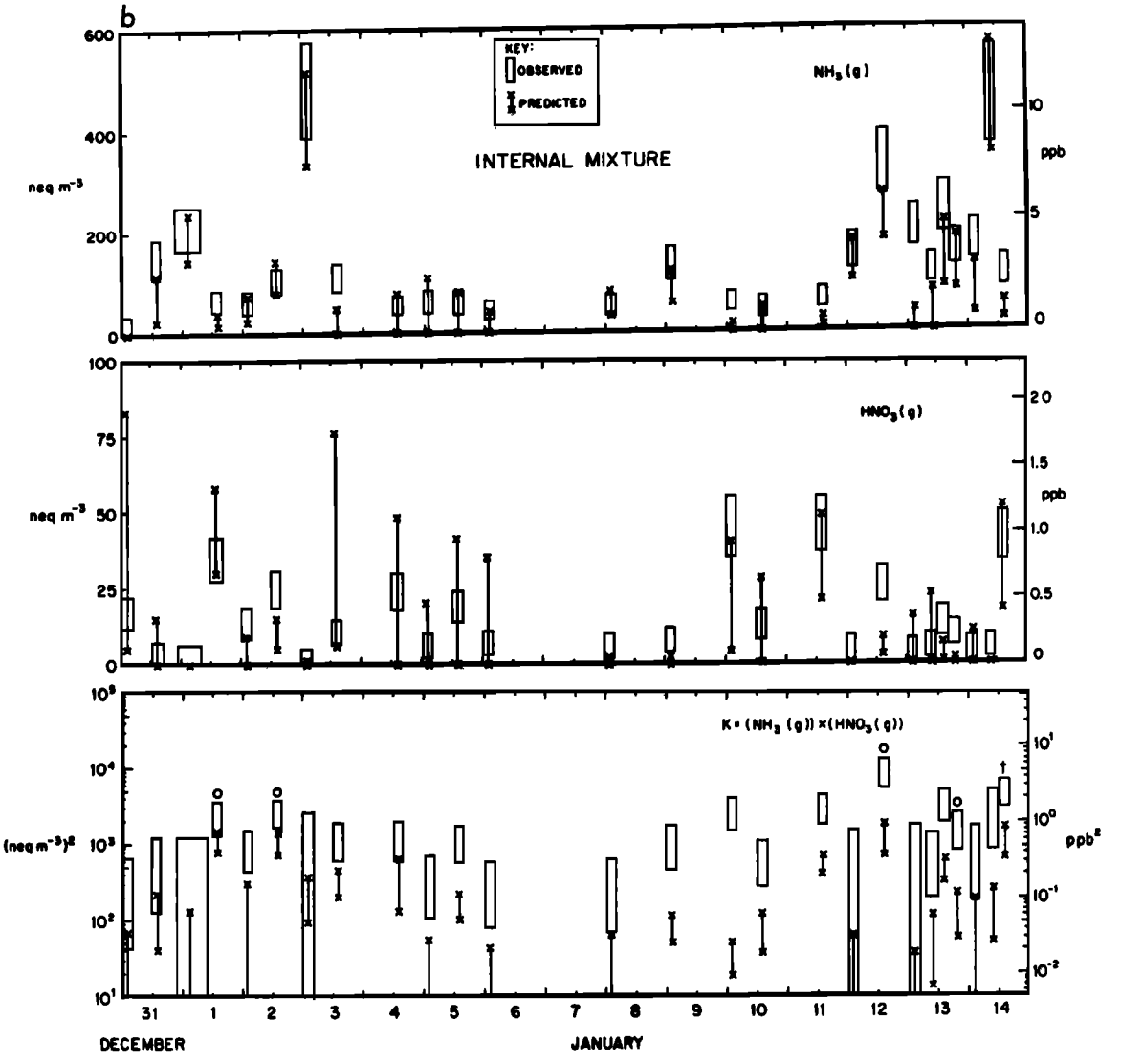

Fig. 2. (continued)

into the aerosol at high humidities proceeds mostly by heterogeneous condensation, which can be a slow process. Based on the calculations of *Fuchs and Sutugin* [1971] over a range of representative conditions, one finds that the diffusion-controlled equilibration time of a gas with low vapor pressure may range from minutes to hours (depending, among other things, on the "sticking coefficient" of the gas molecule on the aerosol).

Foggy Conditions

Nine concurrent samples of fog water, $HNO_3(g)$, and $NH_3(g)$ were collected during the winter 1983–1984 San Joaquin Valley sampling program at Bakersfield and several other sites, and 19 more samples were collected in a similar program conducted the following winter. All samples were collected during intervals with dense fog throughout. The data are given in Table 3. Concentrations of $NH_3(g)$ at equilibrium with the fog water were calculated from (R2) and (R3):

$$(NH_3(g)) = \frac{1}{RTK_2K_3}[NH_4^+]/[H^+] \qquad (2)$$

where $[NH_4^+]$ and $[H^+]$ are the fog water concentrations (equivalents per liter of water), and $(NH_3(g))$ is the $NH_3(g)$ concentration (equivalents per liter of air). The standard errors on predicted $(NH_3(g))$ were determined from standard errors of $\pm 1°C$ on temperature and 15% on the determinations of $[NH_4^+]$ and $[H^+]$ [*Jacob et al.*, this issue]. Several fog water samples were generally collected over the course of one $NH_3(g)$-sampling period; equilibrium $NH_3(g)$ concentrations were calculated from the fog water concentrations in each individual sample and then time averaged. Results are shown in Table 3 and Figure 3.

The $NH_3(g)$ concentrations calculated from (2) were consistent with observed $NH_3(g)$ concentrations in 22 of the 28 comparisons: they agreed to within a factor of 2 for $NH_3(g)$ concentrations above the detection limit (nine cases) and correctly predicted $NH_3(g)$ concentrations below the detection limit (13 cases). In the remaining six comparisons, however, the agreement was poor. Nonattainment of equilibrium is an unlikely explanation for the observed discrepancies; equilibrium of $NH_3(g)$ with fog water at $pH > 5$ is achieved rapidly because of the relatively low solubility of NH_3 [*Chameides*, 1984]. Also, see discussion by *Jacobs* [1985*b*] and *Chameides* [1985]). However, a major source of error in our calculations is that the fog droplets collected in a fog water sample were not of uniform composition. Fog droplets supporting a

TABLE 3. Concentrations of HNO_3(g) and NH_3(g) in Fogs

Date	Temperature, °C	HNO_3(g)/NH_3(g) Sampling Period, PST	Fog Water Sampling Periods	pH[a]	NH_4^+,[a] μeq L^{-1}	NH_3(g)[b] Predicted, neq m^{-3}	NH_3(g) Observed, neq m^{-3}	HNO_3(g) Observed, neq m^{-3}
			Bakersfield					
Jan. 13, 1984	4	0000–0400	0130–0200	6.38	3190	370 ± 86	208	4[c]
			0200–0300	5.92	2800			
			0300–0330	6.72	5920			
			0330–0400	6.74	3300			
Dec. 28, 1984	4	0000–0225	0035–0115	6.80	2680	309 ± 73	363	N/A
			0130–0215	6.20	2780			
Jan. 2, 1985	3.5	2115–0000	2100–2300	6.20	1100	38 ± 15	<25	<6
			2300–0000	5.60	1990			
Jan. 3, 1985	4	0000–0300	0000–0200	5.72	1340	19 ± 7	39	<6
			0200–0305	5.66	1290			
Jan. 3, 1985	2	0300–0700	0305–0500	4.30	781	64 ± 30	262	<4
			0530–0700	6.83	928			
Jan. 3, 1985	1	0700–0930	0700–0830	6.82	1070	161 ± 47	118	<7
			0830–0930	6.51	2900			
Jan. 3–4, 1985	−1	2300–0155	2300–0000	7.08	592	143 ± 42	91	<6
			0000–0100	7.57	379			
			0124–0155	6.76	268			
Jan. 4, 1985	3	2000–2255	2010–2100	6.26	946	22 ± 7	40	<6
			2100–2130	5.16	1340			
			2200–2300	5.46	1440			
Jan. 4–5, 1985	3.5	2310–0205	2300–0000	5.55	1860	11 ± 3	<25	<6
			0000–0100	5.20	1770			
			0100–0200	5.10	1850			
Jan. 5, 1985	2	0400–0805	0400–0500	4.96	1500	7 ± 3	<17	<4
			0500–0600	5.92	1080			
			0600–0700	4.80	1660			
			0700–0800	4.52	720			
Jan. 14, 1985	4.5	0130–0430	0130–0230	6.17	2430	165 ± 45	<25	N/A
			0230–0330	5.56	2390			
			0330–0430	6.72	2170			
Jan. 18, 1985	4	2015–2315	2005–2105	5.85	2400	14 ± 7	<25	9
			2105–2200	4.85	1710			
			2200–2300	4.18	1610			
Jan. 19, 1985	4	0000–0300	0000–0100	3.99	1450	<1	<25	9
			0100–0200	3.86	1450			
			0200–0300	3.67	1590			
Jan. 20, 1985	4	0720–0940	0715–0800	3.06	3130	<1	<29	23
			0800–0845	3.06	3360			
			0845–0930	2.92	3500			
			McKittrick					
Jan. 5, 1984	5	0045–0415	0005–0100	4.02	399	<1	<19	<5
			0100–0200	4.00	347			
			0200–0300	4.02	344			
			0300–0435	4.21	357			
Jan. 6, 1984	5	0000–0410	0035–0100	4.23	241	<1	<16	7
			0100–0200	4.03	294			
			0200–0300	4.22	499			
			0300–0400	4.20	333			
			0400–0500	4.14	345			
Jan. 7, 1984	5	0000–0415	0000–0100	3.96	136	<1	<16	9
			0115–0150	4.41	186			
			0200–0300	4.26	162			
			0300–0400	4.40	204			
			0400–0500	4.44	166			
Jan. 7, 1984	5	1200–1615	1030–1230	4.23	683	<1	<16	11
			1230–1440	4.24	870			
			1440–1540	4.28	740			
			1540–1655	4.12	522			
Jan. 8, 1984	5	0000–0410	2035–0035	4.18	599	1 ± 1	<16	5
			0035–0205	4.50	555			
			0205–0405	5.01	658			
Jan. 10, 1984	5	0045–0445	0010–0120	3.71	845	<1	<17	10
			0120–0525	3.85	351			
			Buttonwillow					
Jan. 7, 1984	6	0100–0500	0040–0140	5.18	1270	10 ± 4	69	4[c]
			0140–0410	5.40	969			
			0410–0620	5.33	1070			
Jan. 3, 1985	4	0000–0220	0000–0215	5.25	2080	11 ± 4	159	<7
Jan. 4, 1985	3	0020–0220	0015–0215	5.73	553	8 ± 3	42	<8
Jan. 4, 1985	1.5	0415–0810	0430–0630	6.14	519	16 ± 6	<17	<4

TABLE 3. (continued)

Date	Temperature, °C	$HNO_3(g)/NH_3(g)$ Sampling Period, PST	Fog Water Sampling Periods	pH[a]	NH_4^+,[a] μeq L^{-1}	$NH_3(g)$[b] Predicted, neq m^{-3}	$NH_3(g)$ Observed, neq m^{-3}	$HNO_3(g)$ Observed, neq m^{-3}
			Buttonwillow (continued)					
Jan. 4, 1985	4	1930–2135	1930–2030	6.55	968	124 ± 33	79	N/A
			2030–2135	6.76	858			
Jan. 5, 1985	2.5	0220–0410	0205–0300	5.70	529	8 ± 2	102	<9
			0300–0400	5.87	483			
Jan. 5, 1985	2	0415–0810	0400–0500	6.16	456	75 ± 21	145	<8
			0500–0615	6.78	683			
			0615–0700	6.89	582			
			0700–0800	6.87	542			
			Visalia					
Jan. 7, 1984	6	0145–0335	0120–0250	6.97	860	355 ± 90	592	<8
			0250–0430	7.23	678			

Measurement errors for $NH_3(g)$ and $HNO_3(g)$ were about 20%. Detection limits depended on filter run time [*Jacob et al.*, this issue]. N/A = not analyzed.

[a]Fog water concentrations. Complete fog water analyses are reported by *Jacob* [1985*a*] for the January 1984 data and by *Waldman* [1986] for the December 1984 to January 1985 data.

[b]Average over time of $NH_3(g)$ concentrations predicted from fog water concentrations and equation (2).

[c]Detection limit.

measurable partial pressure of NH_3 contain alkalinity, and $[H^+]$ will not be conserved upon the mixing of alkalinity-containing droplets of different compositions in the sample. Further, $(NH_3(g))$ is proportional to $1/[H^+]$, a quantity which is not properly averaged by measurement of *p*H in the collected sample. The resulting errors will depend on the extent of nonuniformity in the fog water composition and are difficult to estimate, but they could clearly account for most of the discrepancies. The large variations in *p*H often observed between two consecutive fog water samples (Table 3) are indicative of the variability in fog water composition.

The largest discrepancies were observed for four sampling periods at Buttonwillow when the fog water *p*H was in the range 5–6. In those four cases, equilibrium with fog water considerably underpredicted the observed $NH_3(g)$ concentrations. Fog water at *p*H 5–6 scavenges most of the atmospheric NH_3 (Figure 1) but returns it to the gas phase upon evaporation [*Jacob et al.*, this issue]. An explanation for the large discrepancies that were sometimes observed in this *p*H range is the existence within the fog of pockets of air undersaturated with respect to water vapor [*Gerber*, 1981]. These air pockets would support much larger concentrations of $NH_3(g)$ than the bulk foggy atmosphere and would correspondingly affect the measured $NH_3(g)$ concentration. Further, sampling of undersaturated air may evaporate fog droplets previously collected on the aerosol prefilter and cause artifact $NH_3(g)$.

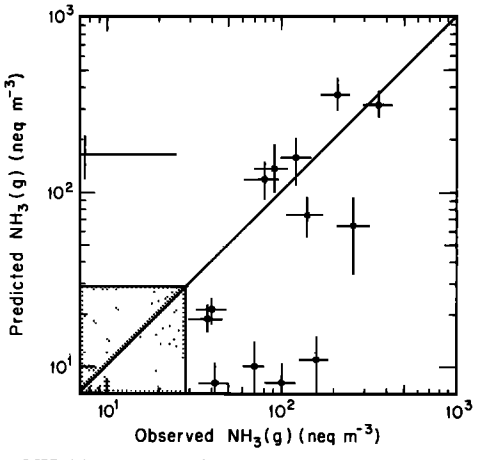

Fig. 3. $NH_3(g)$ concentrations at equilibrium with fog water versus observed $NH_3(g)$ concentrations. Both were below the detection limit for 13 of the points (shaded area). Line represents 1:1 agreement between predictions and observations.

Concentrations of $HNO_3(g)$ in fogs were at or below the detection limit in fogs with *p*H > 5, but detectable $HNO_3(g)$ concentrations (5–23 neq m^{-3}) were found in fogs with lower *p*H. The presence of $HNO_3(g)$ in acidic fog cannot be explained on the basis of equilibrium with fog water. However, the presence of $HNO_3(g)$ can be explained by the substantial vapor pressure of $HNO_3(g)$ over the acid precursor aerosol; undersaturated air pockets within the fog would support $HNO_3(g)$ at equilibrium. An additional explanation is that detectable $HNO_3(g)$ concentrations may subsist for some time in the fog because of the slow rate of $HNO_3(g)$ diffusion to the droplets. *Chameides* [1984] reports that scavenging of $HNO_3(g)$ by diffusion to the fog droplets proceeds on a time scale of a few minutes, but this time may be longer if organic films form at the surface of the droplets [*Gill et al.*, 1983].

CONCLUSION

Concentrations of $HNO_3(g)$ and $NH_3(g)$ were determined in the field under both foggy and nonfoggy conditions, simultaneously with aerosol and fog water composition. Observed concentrations were compared to predictions from thermodynamic models.

Measurements under nonfoggy, cool, and humid conditions (temperatures 3°–13°C, relative humidities 60–100%) were compared to predictions from the *Bassett and Seinfeld* [1983] model for the H_2SO_4-HNO_3-NH_3-H_2O system. The observed products of HNO_3 and NH_3 vapor pressures were of the same magnitude as those predicted by the model; however, the model predictions were consistently too low. The agreement between observations and model was slightly improved by assuming that SO_4^{2-} and NO_3^- were present in different phases (external mixture).

Concentrations of $NH_3(g)$ were below the detection limit of 17–30 neq m^{-3} in fogs with *p*H < 5, and this is consistent with thermodynamic predictions. Substantial $NH_3(g)$ concentrations were observed in fogs with higher *p*H; the observed concentrations were usually within a factor of 2 of those predicted at equilibrium with the fog water, but some

important discrepancies were noted. These discrepancies may be due to fluctuations in fog water composition over the course of sample collection or to the presence of pockets of undersaturated air within the fog.

Concentrations of $HNO_3(g)$ were at or below the detection limit of 4–8 neq m^{-3} in fogs with $pH > 5$, but detectable concentrations (5–23 neq m^{-3}) were often found in fogs with lower pH. Because $HNO_3(g)$ should not be present at equilibrium with fog water, we attribute our observations to the presence of undersaturated air within the fog or to the slow rate of $HNO_3(g)$ diffusion to the fog droplets.

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